U.S. DEPARTMENT OF ENERGY
Fossil Energy and Carbon Management

Beyond Combustion – Coal in the 21st Century

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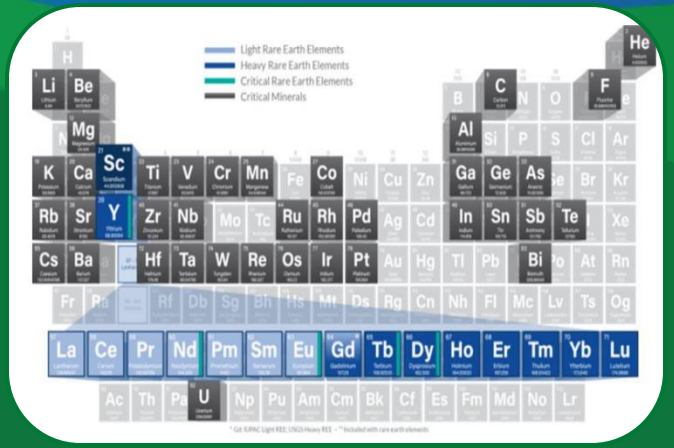


Carbons from Coal

Many Possibilities

- Activated Carbons
- Coke
- Chars
- Graphite and Carbon Electrodes
- Graphene
- Nanocarbons
- Composites and Alloys
- Carbon Fibers, Blocks, Roof Shingles, Deck Boards, Pipes
- Carborundum (Silicon Carbide), Diamond

Program Overview

- Current Projects (35) – Covering Building Materials (Bricks, Blocks, Deck Boards, Roof Shingles), Silicon Carbide, Beneficiation, Graphite, Carbon Fibers, Nanomaterials
- Completion of Current Projects
- Focus on Clean Energy High Value Materials
- High Volume Materials
- Graphite is a Critical Material
- Use of Byproduct Carbons from Critical Material Recovery
- Many Synergies with Critical Materials Program

Motivation for the Program

- Develop Clean Energy & Novel High Value Carbon Products to Incentivize and Facilitate Clean-Up of Waste Coal and Coal Byproduct Impoundments
- Use of Byproduct Carbons from Critical Material Recovery
- Focus on Clean Energy & Highest Value Products Such as Graphene, Nanocarbons, Graphite, Battery Electrodes, Specialty High Surface Area Activated Carbons, Novel Alloys, Fibers
- Develop High Volume Products Such as Building Materials
- Bricks, Blocks, Roof Shingles, Pipes, Deck Boards

What is Coal?

Lignite

Subbituminous

Bituminous

Anthracite

Low-ranking → High-ranking

Classic Analysis – Moisture, Volatile Matter, Fixed Carbon, Ash

Sequentially Dry, Pyrolyze and Burn Coal

Weight Loss From Each Step Yields – Moisture, VM, FC, and Ash (balance)

Source: Zazzeri, G. et al. (2016). *Atmos. Chem. Phys.* (16), 13669-13680. 10.5194/acp-16-13669-2016., Adapted from https://creativecommons.org

Coal Classifications

ASTM Coal Classification by Rank (*2*)

Class and group	Fixed carbon, %	Volatile matter, %	Heating value, Btu/lb
I. Anthracitic			
1. Metaanthracite	>98	<2	
2. Anthracite	92–98	2–8	
3. Semianthracite	86–92	8–14	
II. Bituminous			
1. Low volatile	78–86	14–22	
2. Medium volatile	69–78	22–31	
3. High volatile A	<69	<31	>14,000
4. High volatile B			13,000–14,000
5. High volatile C			10,500–13,000
III. Subbituminous			
1. Subbituminous A			10,500–11,500
2. Subbituminous B			9,500–10,500
3. Subbituminous C			8,300–9,500
IV. Lignitic			
1. Lignite A			6,300–8,300
2. Lignite B			<6,300

Graphitization in Nature – Coal and Graphite

Table 2. Variations of Physical and Chemical Properties with Rank and Their Useful Range as Rank Parameters [c]

Classification	% C (daf)[a] of Vitrinite	Vol. Matter % daf[a]	Moisture % in Situ	Cal. Value BTU/LB (af)[b]	Reflectance % (Vitrinite)	Important Characteristics
Peat	60		75			1. Free Cellulose 2. Plant Detail Recognizable
Soft Brown Coal		53	35	7,200	~0.3	1. No Free Cellulose 2. Plant Structure Recognizable
Lignite	~71	49	25	9,900		1. Plant Structure Still Partly Recognizable 2. Vitrinite Formed
Subbituminous	77	42	8–10	12,600	~0.5	Low-Reflecting Exinite
High Volatile Bituminous	87	29		15,500	1.1	Exinite Lighter in color Exinite Vitrinite Indistinguishable
Med Vol. Bit. Low Vol. Bit. Semi-Anthracite	91	8		15,000	2.5	Anisotropic Reflectance
Anthracite Meta Anthracite Graphite	100	0				

Increasing Rank

Applicability of Properties as a Rank Parameter:
- % C daf,[a] Reflectance of Vitrinite
- Volatile Matter daf[a]
- X-Ray Diffraction
- Calorific Value (af)[b]
- % H daf[a]
- % Moisture in Situ

[a] daf—Dry Ash Free
[b] af—Ash Free
[c] Adapted from: "Coal and Coal Bearing Strata," (*Editors:* D. Murchison and T. S. Westall), and "The International Handbook of Coal Petrography," International Committee for Coal Petrology

Graphitization in Nature – Coal and Graphite

Table 1. Coal and Coal-Related Carbonaceous Materials in Nature (from Schobert 1989)

Muck

Peat

Lignite  closer to surface  increasing age, fixed carbon & graphitization

Subbituminous Coal

Bituminous Coal

Anthracite

Graphitization in Nature – Coal and Graphite

Graphite Formed in Nature

- Elevated Temperatures/Pressures
- Or Contact with Hot Magmatic Fluids
- Typically, Over Eons ("Coalification/Graphitization")
- Muck – Peat - Lignite – Subbituminous – Bituminous – Anthracite – Meta Anthracite – Graphite
- "The Geochemistry of Coal – Part I. The Classification and Origin of Coal", Harold H. Schobert, Journal of Chemical Education, 242-244, 1989.
- "The Geochemistry of Coal – Part II. The Components of Coal", Harold H. Schobert, Journal of Chemical Education, 290-293, 1989.

Abundant Domestic Coal – U.S. Has World's Largest Reserves

Source: Fletcher & Baylis/Science Source

Estimated Recoverable Reserves

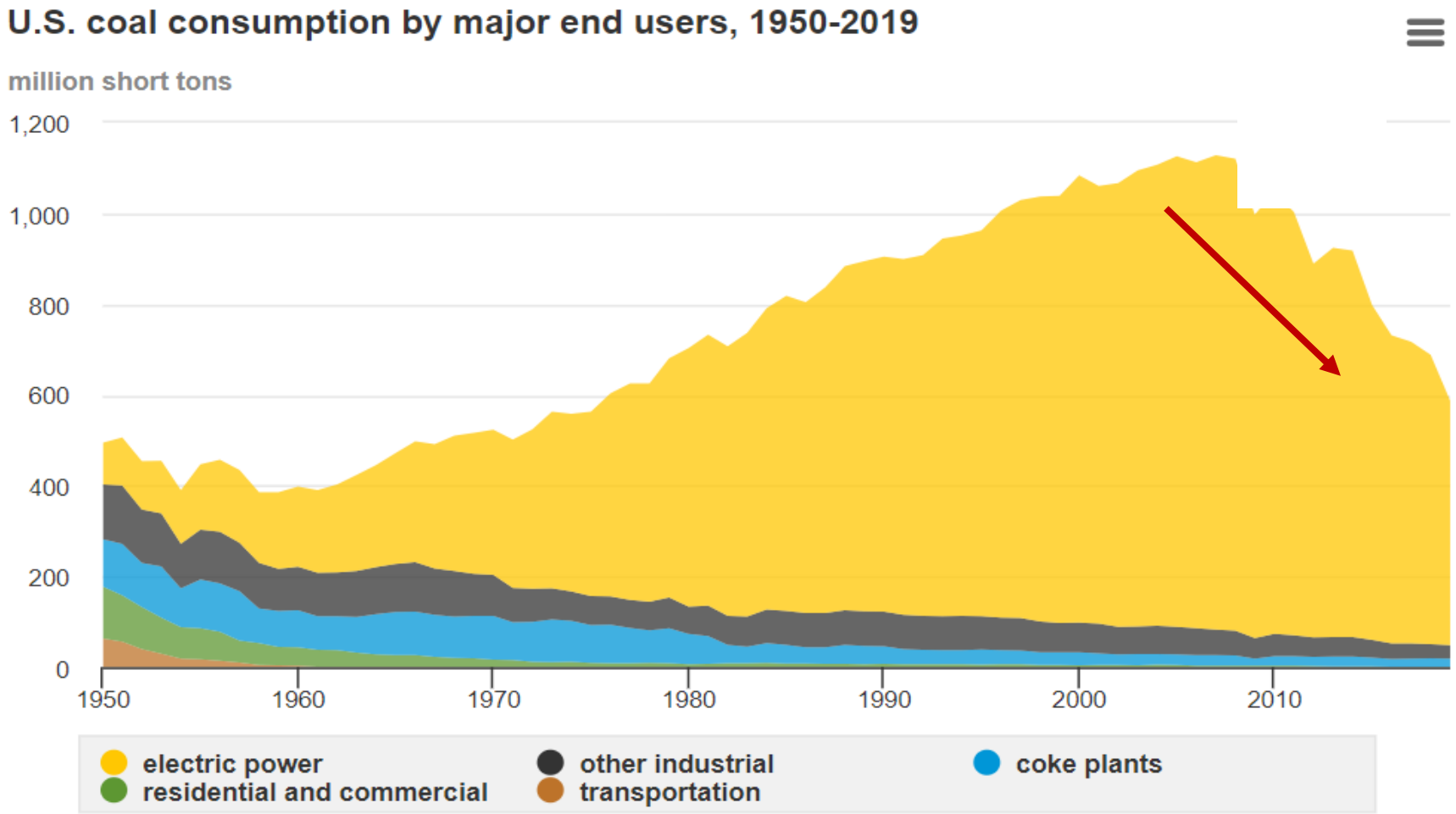
- Coal that can *currently* be mined
- 253 billion short tons

Demonstrated Reserve Base

- Total amount of coal that could *feasibly* be mined
- 474 billion short tons

Declining Domestic Production and Consumption

Trends in U.S. Coal Consumption



Source: U.S. Energy Information Administration, *Monthly Energy Review*, Table 6.2, May 2020

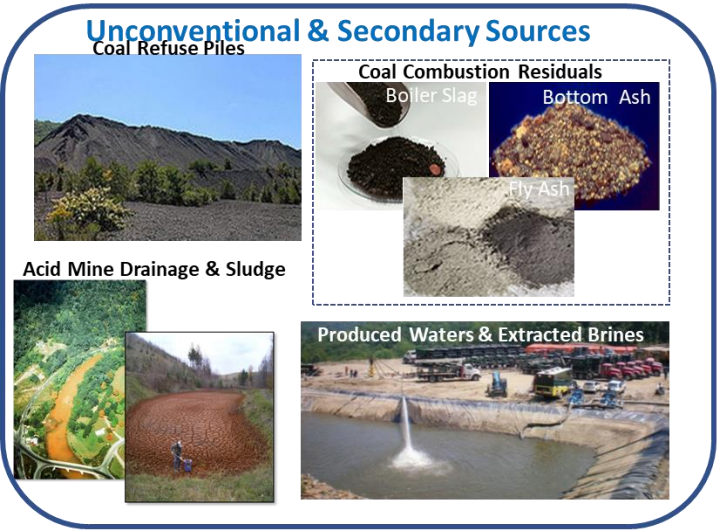
Coal and Waste Coal Resources

- US Has 250-300 Year Supply Coal—World's Largest by a Wide Margin
- Approximately 1 – 1.1 billion tons/year Produced from 1990 – 2014 (EIA)
- 535 Million Tons in 2020; 578 Million Tons in 2021 (EIA)
- US Coal – Most Used for Generation Electricity
- Retirements of Older Coal-Burning Power Plants
- Inexpensive Natural Gas
- Activated Carbons, Chemicals, Tars, Steel, Exports
- We Can Do So Much More with Coal, Waste Coal and Byproducts

Principles of Waste Minimization and Circularity

Reclaiming, recycling waste materials

Maximizing use of feedstock materials



How Do We Process Utilize Coal?

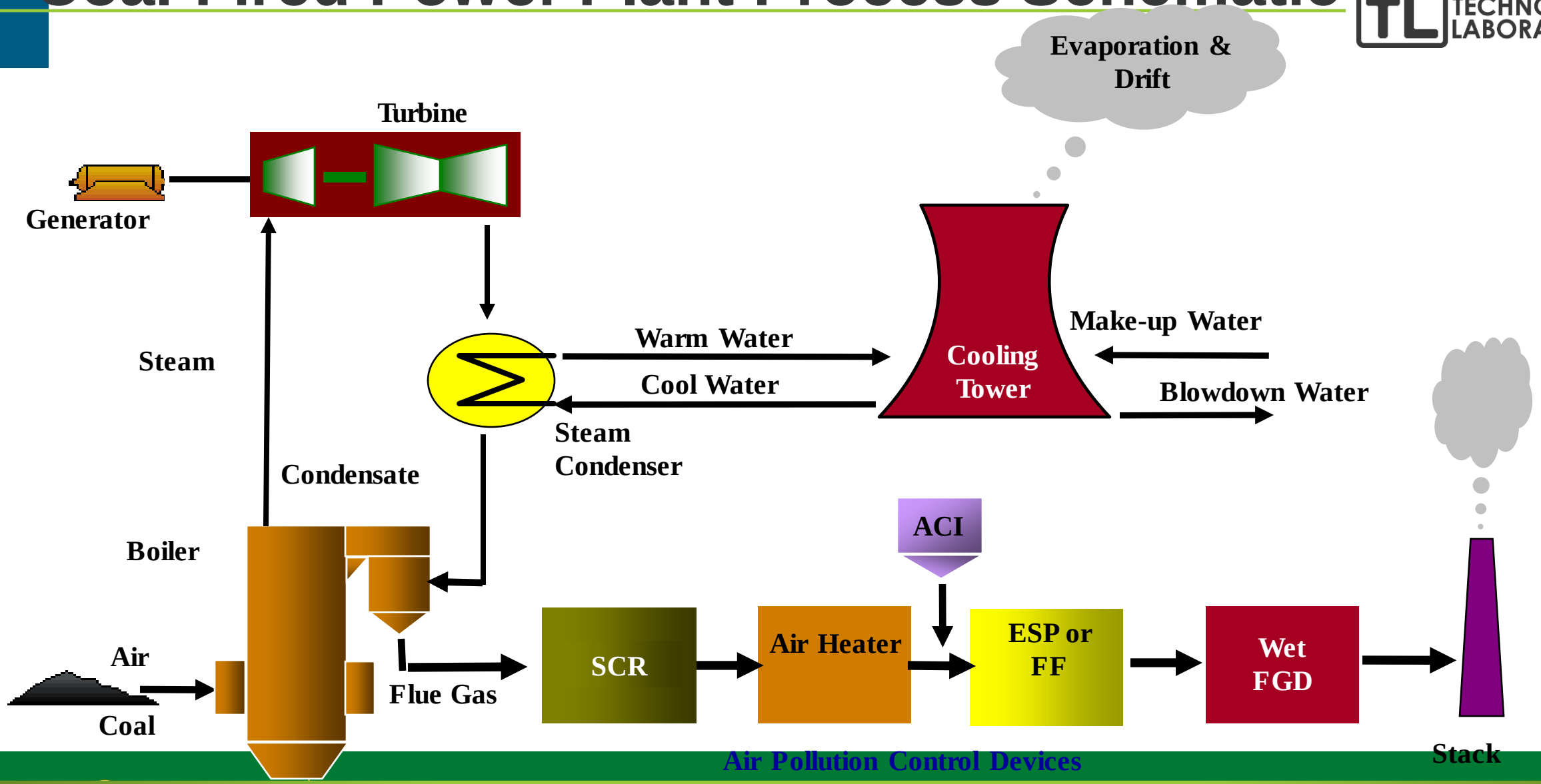
Two Typical Routes

1. Combustion: Power Generation, Heat

2. Pyrolysis and Gasification: Chemicals, Tars, Liquid Fuels, Activated Carbons, Power Generation

Under Carbon Ore – Novel Carbons, Typically by Pyrolysis

Coal-Fired Power Plant Process Schematic



What is Gasification?

Gasification

- Carbon – Steam or Carbon – Carbon Dioxide Reactions
- $C + H_2O \rightarrow CO + H_2$ $C + CO_2 \rightarrow 2\ CO$
- To make Syngas (Fuel Gas)
- Primarily CO and H_2
- Burn to Make Electricity
- Convert to Chemicals and Fuels
- FT Process
- Methanol, Synthetic Gasoline, Waxes,…….

What is Gasification & Fuel Gas (Syngas)?

- Carbon-Steam Reaction
- Pyrolysis – Thermally Neutral
- Combustion
- Elevated Pressure

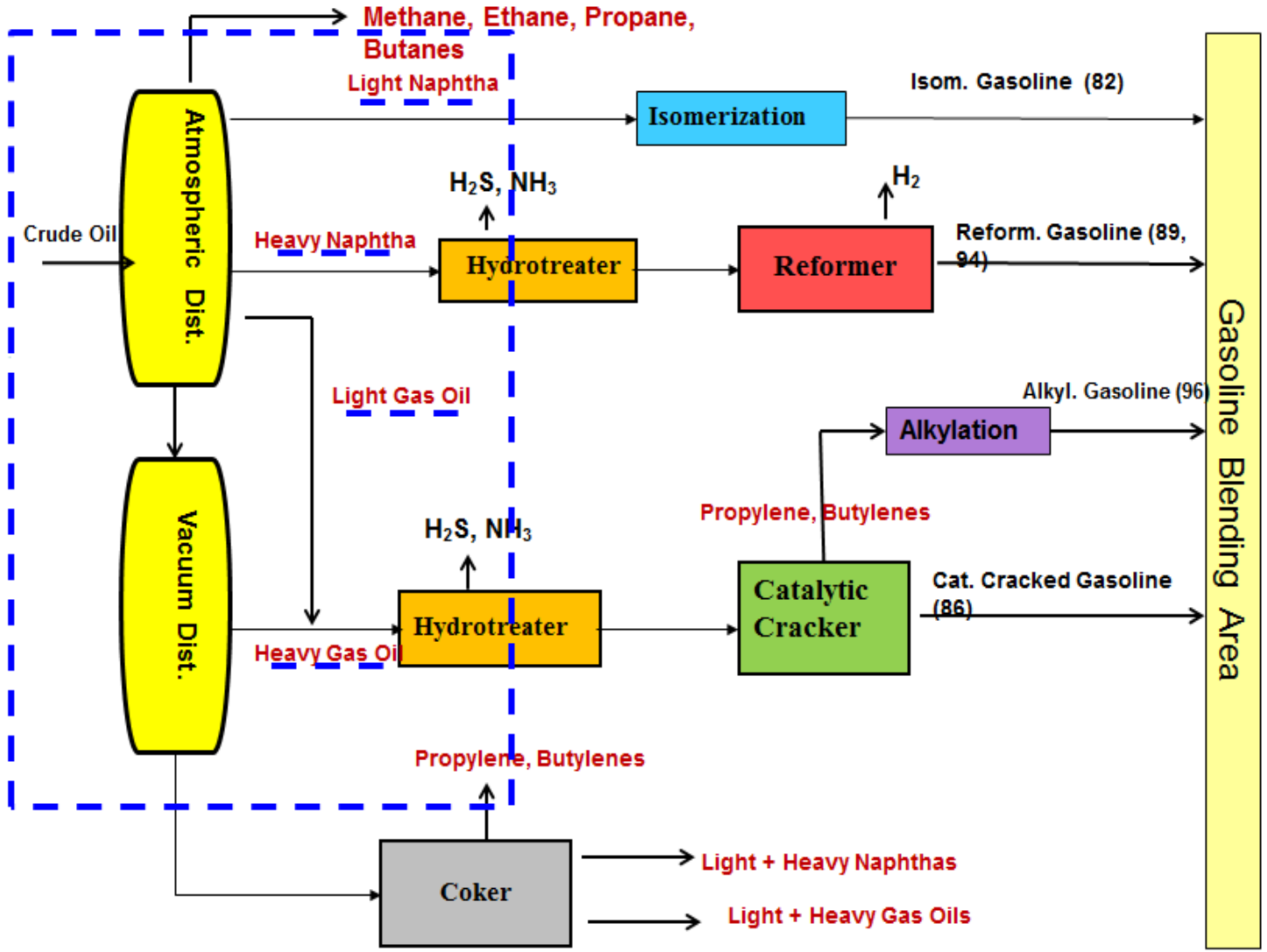
Major Products

- CO, H_2, CO_2, H_2O, Tars & HCs, Chars

Minor Products

- NH_3 , HCl, Cl_2 and particulates
- H_2S, COS, CS_2
- Trace Contaminants: Hg, AsH_3, H_2Se, and PH_3

Petroleum Refinery – Uses Every Part of the Fossil Fuel



ORNL Projects

FWP-FEAA155 – C4AWAR

- "Coal Conversion for Carbon Fibers and Composites"
- 10 MM Graphite, Fibers, and Composites – Lab-Scale R&D

FWP-FEAA157

- "Scale-up Production of Graphite and Carbon Fibers from Coal and Coal Refuse"
- 10 MM Scale-Up at Oak Ridge Carbon Fiber Pilot Facility
- Carbon Fibers Envisioned for Lightweight Automobiles
- Graphite for Batteries (New ORNL Technology for Graphite)

Carbon Ore to Products: Opportunities Toward a Clean Energy Transition

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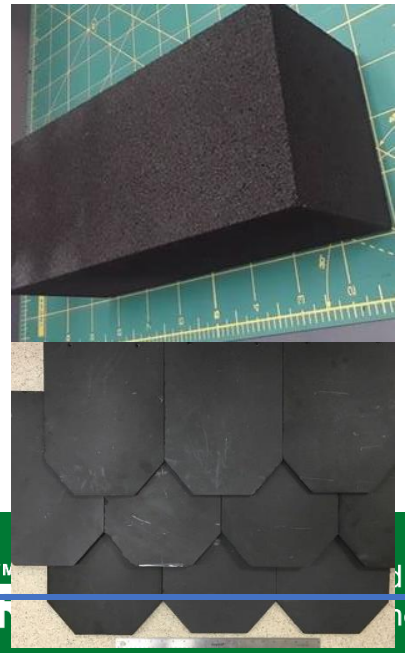
Advanced processing of carbon ore and associated by-products for the development of everyday and high value carbon products

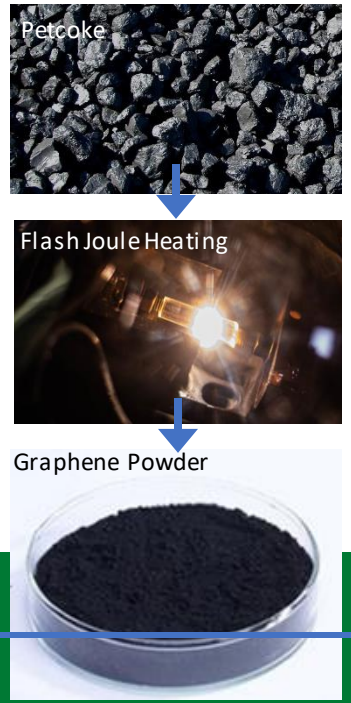
- Generated predominantly from ***coal waste and refuse*** – toward remediation
- Enable domestic manufacturing of strategic materials to encourage job creation
- Ensure the health and safety of the environment and people around the use and disposal of carbon-based products

Next-Gen Construction & Infrastructure Materials

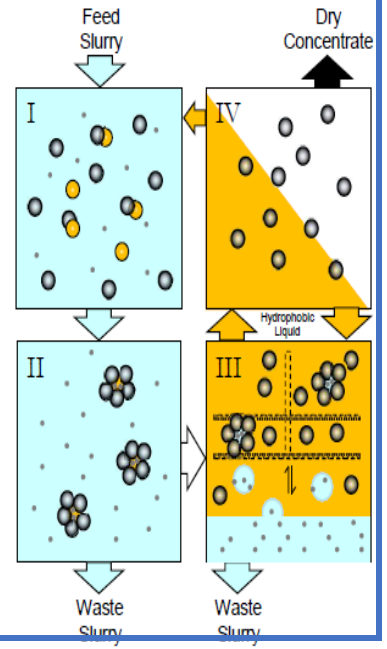


Carbon Fibers from Coal Tar Pitch

Nanomaterials



Waste Recovery



Transformation of Carbon Ore to Graphite

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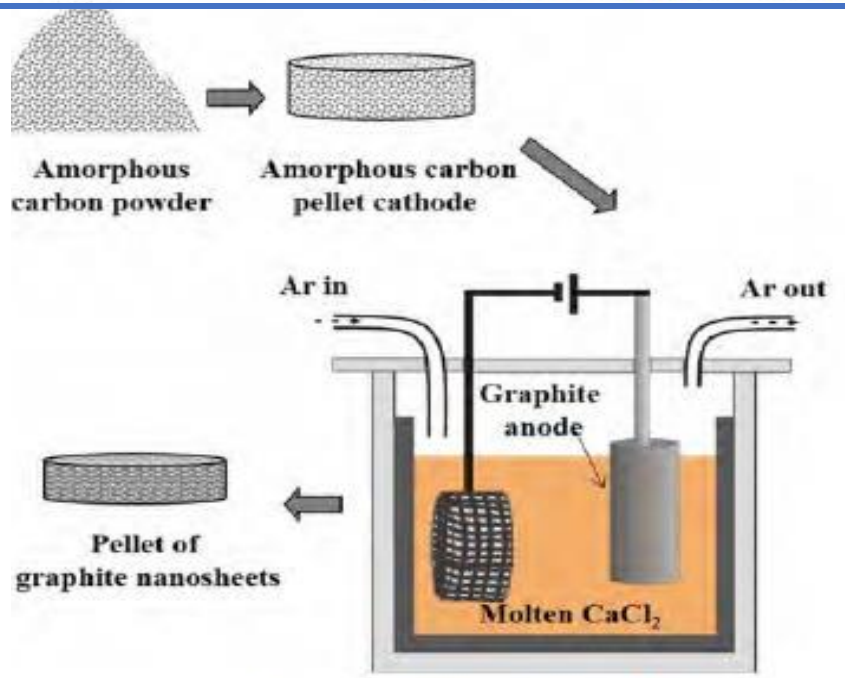
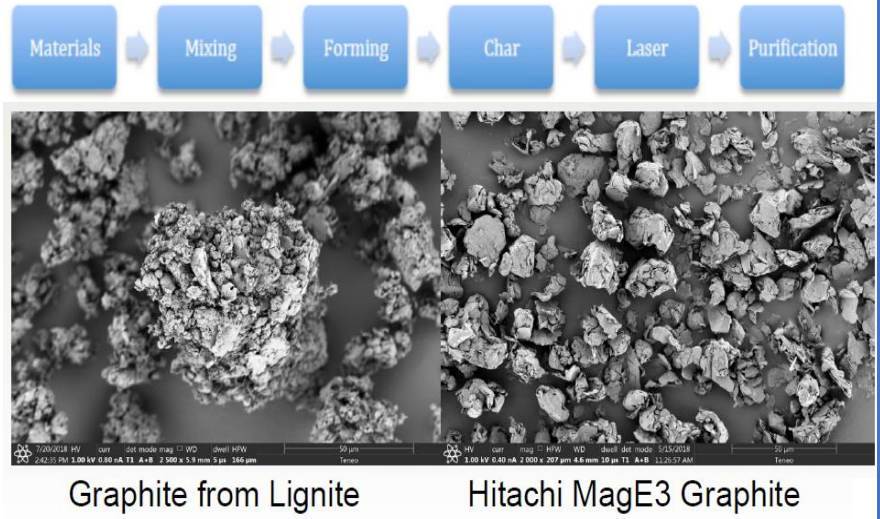
To address anticipated increase in demand, funding research on synthetic graphite



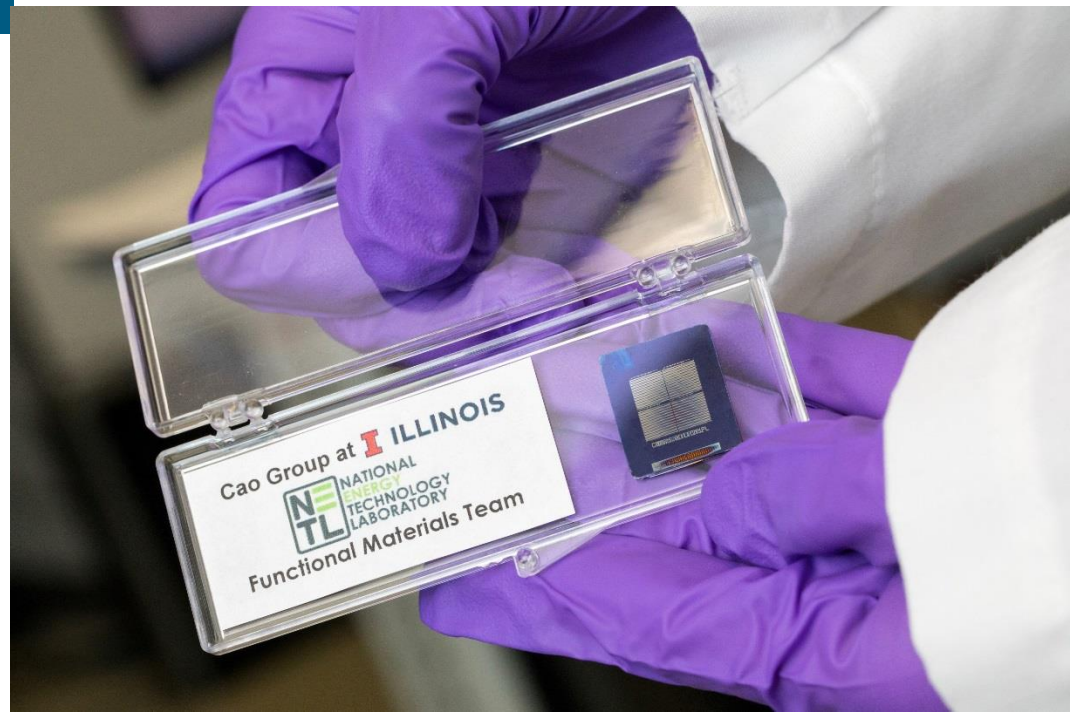
ORNL is investigating the conversion of coal char into graphite using a low-temperature electrochemical graphitization process



George Washington University is researching coal to Li-ion battery grade (potato) graphite

***FOA 2405: "*Advanced Coal Waste Processing**

Carbon Electronics: Memristor Computer Memory



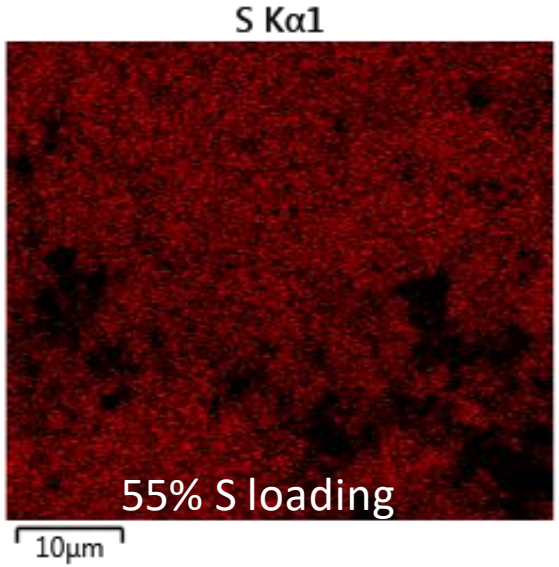
ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Cao Group, Materials Science

- **Memristor computer memory devices:**
  - Emerging memory technology
  - Energy efficient (<pJ/operation)
  - High speed (10 ns)
  - Easily miniaturized (10 X 10 nm)
  - Integrable on logic chip
- **Coal carbons outperform other carbons and metal oxides:**
  - Lower cost fabrication method
  - Improved device-to-device reproducibility
  - Better long-term device stability

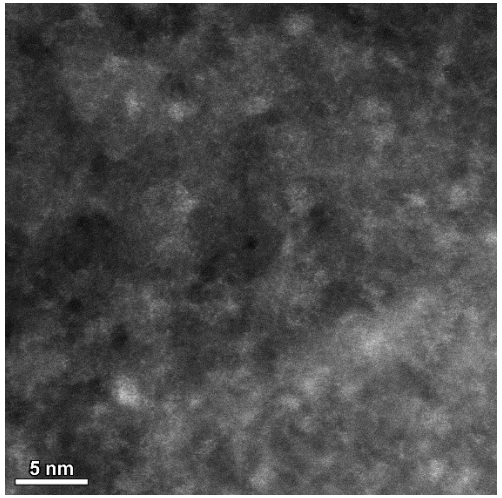
Porous carbons for energy storage, chemical processing, & filtration applications

Energy Storage



- Application: LiS battery
- 25-33% increase in S loading w.r.t. SOTA

Chemical Processing



- Applications: CO_2 Utilization, Chemical processing, synthetic fuels
- Single metal atoms dispersed on carbon
- Unprecedented activity for , H_2 , O_2 , CO, CO_2, organic decomp

Filtration & Membranes

Massachusetts Institute of Technology

- Ideal pore size for water desalination, testing in progress at NETL
- Solid carbon membranes w/MIT

Current Portfolio – Pyrolysis of Coal

Waste Minimization

- Pyrolysis – Heat Coal in Absence of Air
- Outstanding Strategy for Upgrading Coal
- Thermally Neutral : $\Delta H_{\text{Reaction Pyrolysis}} = 0$
- Decomposition of Volatile Matter & Graphitization of Carbon
- Produce Char, Tar and Gases
- Focused Upon Char **or** the Tar (For Carbon or Pitch)
- Results in Wasted Gas, Tar and/or Char
- Future Work – Utilize All of The Pyrolysis Products
- No Wasted Molecules

X-MAT – Tour April 7, 2022

X-MAT – Tour April 7, 2022

FOA 2620

- Released July/August 2022
- AO1: Graphite (Synergy with Critical Materials)
- AO2: Composites and Novel Alloys
- 6 MM Total
- Selections Announced
- https://www.energy.gov/fecm/articles/doe-invests-6-million-develop-useful-products-coal-and-coal-wastes-support-clean
- DOE Invests $6 Million to Develop Useful Products from Coal and Coal Wastes in Support of a Clean Energy Economy
- February 16, 2023

Future Research

a) High Value Products for Clean Energy Economy - Carbon Nanomaterials, Graphite, Specialty Ultra-High Surface Area Activated Carbons (UHSAAC), Fibers, Novel Alloys, Diamonds

b) Utilization of Entire Coal Value Chain – Volatile Matter (Tars and Pitch – Fibers; Gases - Chemicals), Mineral Matter (Critical Minerals), Fixed Carbon (Carbon Nanomaterials, Graphite, UHSAAC) – No Wasted Molecules – Multiple Products - Better Process Economics – Greater Incentive to Clean-Up Coal Impoundments

- Utilize Byproduct Carbons from Recovery of CMs

c) Tracking and Removal of Harmful Trace and Minor Element Species – Zero Emissions

Annual Review Meeting

- Downtown Pittsburgh
- In Person
- October 2022
- Over 40 Presentations on Carbon Ore Research
- Presentations are Available On-line
- https://netl.doe.gov/22RS-proceedings

Acknowledgements

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- Mary Anne Alvin
- Savannah Rice
- Acqueetta Ragland-Higdon

Additional Information

- Much additional information is available on the NETL Carbon Ore website:
- https://netl.doe.gov/Carbon-Ore-Processing

- A factsheet is also available:
- https://netl.doe.gov/sites/default/files/2022-11/Program-151_0.pdf

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Fossil Energy and Carbon Management

Questions

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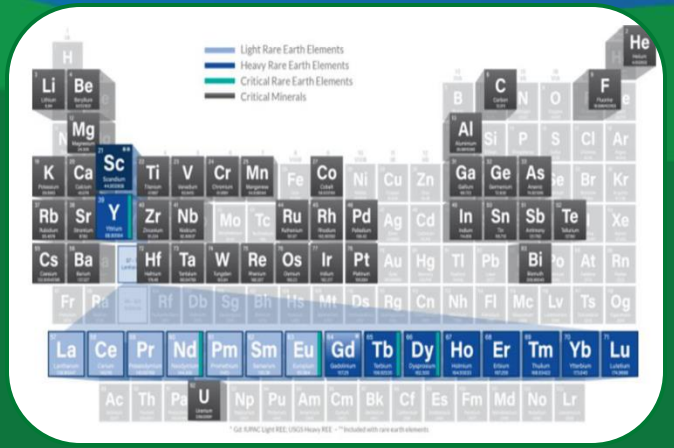

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